AD A103218

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A103218	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Electron Impact Cross Sections Applicable to Molecular Lasers		5. TYPE OF REPORT & PERIOD COVERED Summary 11/10/79 - present
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Shek-Fu Wong		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0078
9. PERFORMING ORGANIZATION NAME AND ADDRESS Yale University Mason Laboratory, P.O. Box 2159 Yale Station New Haven, CT 06520		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 394-003
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Physics Program Office (Code 421) Arlington, VA 22217		12. REPORT DATE August 1981
		13. NUMBER OF PAGES 2
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

DTIC
AUG 24 1981

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Dissociative Attachment; 0-4 eV; Cross Sections
Vibrationally Excited Molecules; New Mechanisms

Electronic Excitation; 4 eV within Threshold
Differential Cross Sections; Resonances

Cl^-/HCl^* ; F^-/HF^*

He: 2^3S, 2^1S, 2^3P, 2^1P
Ar: $^3P_{2,1,0}$

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

ELECTRON IMPACT CROSS SECTIONS APPLICABLE TO MOLECULAR LASERS

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Ref: Contract N00014-76- C-0078

Summary

1. Contract Description:

This program centers on the measurement of electron impact cross sections of basic importance to the collision mechanisms in molecular lasers. The investigations include dissociative attachment, vibrational and electronic excitation in selected molecules and atoms, at low impact energies.

2. Scientific Problem:

Inelastic collisions between electrons and molecules proceed via direct and resonant processes. It is important to establish the relative contribution of these two mechanisms. This goal can be achieved by studying the energy and angular dependences of the scattering cross sections. A systematic study of the resonances by their energy, lifetime and symmetry also helps to form an overall physical picture of the mechanisms whereby the electron energy is transferred to the target molecule or atom.

3. Scientific and Technical Approach:

We use several distinct methods for studying the cross sections of interest. A hemispherical electron impact spectrometer is used for vibration excitation and electronic excitation studies from ground or vibrationally excited molecules. An electron impact mass spectrometer is used for dissociative attachment studies with target gas at temperature up to 1600 $^{\circ}$K. Our data acquisition and analysis systems include 2 PDP-11/MINC computers. A new kind of ion impact spectrometer for electron and ion collisions at high resolution and low incident energies has recently been developed here and is currently in operation.

4. Specific Objective:

a) Electronic Excitation in Noble-Gas Atoms. To continue our studies on the differential cross sections of the lowest $4\,^3P_2$, $4\,^3P_1$, and $4\,^3P_c$ states in Ar, withinin 4 eV of their thresholds. Efforts are focussed on the branching ratios, magnitude and nagular behaviour of these cross sections. Kr will be the next.

b) Collisional Detachment of Cl^- and O^-. To do survey experiments with Cl^- and O^- on various target atoms and molecules, at impact energies 10^{-1} to 10^1 eV. Efforts will be directed to quantitative measurement of the energy and angul r distribution of the detached electrons. Such data are vital to understanding the mechanism of collisional detachment, but are hitherto unavailable from the other existing methods.

5. Progress Since November 1979:

In the program on excited molecules we have completed the experiments on dissociative attachment from vibrationally excited HCl and HF. In this work we observed an unusually large cross section (10^{-14} cm^2) for $Cl^-/HCl(v=2)$ and proposed a new mechanism for dissociative attachment by electron impact. These results have been published in Journal of Chemical Physics, 1981.

In the program on electronic excitation of noble-gas atoms we have established the experimental methods for studies up to the threshold region. The first results have been obtained for the n=2 states of He, within 4 eV of threshold. In the 2^3S and 2^3P cross sections we observed anomalous angular dependences attributable to a new ^2P resonance. These results have been published in Physical Review A, 1981. A PhD thesis also resulted from the He work and an initial experiment on Kr.

I have carried out the first electronic excitation experiments in Ar ($4^3P_2, 4^3P_1, 4^3P_0$) with a newly constructed ion impact spectrometer operated in electron scattering mode. Angular and energy dependences of these 3 triplet cross sections are determined within 4 eV of threshold. The Ar experiments also led to the O^-/Kr and Cl^-/Kr experiments, which show that collisional detachment at low impact energies yields mainly very slow electrons, with kinetic energy less than 1 eV. These preliminary findings have been presented in an invited talk at the Goddard Symposium on electron scattering from atoms and atomic ions, Greenbelt, July 1981.

6. Publications:

J. M. Phillips and S. F. Wong, "Electron-impact excitation of He: Threshold region", Phys. Rev. A23, 3324 (1981).

M. Allan and S. F. Wong, "Dissociative attachment from vibrationally and rotationally excited HCl and HF", J. Chem. Phys. 74, 1687 (1981).

S. F. Wong, "New Experiments on e-He, e-Ar Resonances", NASA Goddard Symposium on Electron Scattering from Atoms and Atomic Ions, Greenbelt,(1981).

7. Associated Personnel:

J. M. Phillips (Graduate Student)
M. Allan (Postdoctoral)
J. H. Kearney (Technical Staff)

8. Other Sources of Support:

NSF "Resonant Processes in Electron Scattering"
1 April 1980 - 30 September 1981, $89,151
Extension applied.

Dissociative attachment from vibrationally and rotationally excited HCl and HF[a]

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An electron impact mass spectrometer is used to study dissociative attachment in HCl, DCl, and HF at incident energies 0–4 eV. Target molecules in different excited nuclear states are prepared with an iridium oven source. The cross sections for Cl^-/HCl, Cl^-/DCl, and F^-/HF all show an order-of-magnitude increase with each increase of vibrational quantum ($v = 0$, 1, and 2). In Cl^-/HCl the threshold cross section for the $v = 2$ level at 0.1 eV reaches $(7.8 \pm 4.7) \times 10^{-15}$ cm^2. Together, this large cross section and the recent potential-energy-curve calculations of HCl and HCl^- show that the conventional theory of dissociative attachment may not be applicable here. A new mechanism for dissociative attachment is suggested.

I. INTRODUCTION

Electron collisions with excited molecules are of basic interest as well as having interdisciplinary applications.[1] In dissociative attachment by electron impact, the important role of nuclear excitation was first observed via the marked dependence of cross sections on temperature. This effect was studied in several molecules (O_2, N_2O, CO_2 ...) and has been reviewed.[2]

Recent improvements in electron-beam resolution and ion detection have enabled us to study[3] dissociative attachment from specific vibrational and rotational states in H_2 and D_2. At electron energies 1–4 eV, the cross section was found to increase drastically, by more than a factor of ten, with each vibrational quantum. A weaker enhancement was observed with rotational quantum. These results, together with a quasi-stationary-state calculation by Wadehra and Bardsley[4] brought understanding to the *detailed* roles of excited nuclear states. Dissociative attachment in H_2 and D_2 proceeds via the repulsive action of a short-lived $^2\Sigma_u^+$ resonance.[5] The enhancement in cross section arises predominantly from the shortening of stabilization time for dissociation. In vibrationally excited molecules this is due to the more extended nuclear wave function; in rotationally excited molecules to the centrifugal stretching.

To gain further understanding we have recently extended similar investigations to two hydrogen halides, HCl and HF. HCl and HF possess large electric dipole moments (1.11 and 1.82 D), thereby introducing a strong long-range force not normally encountered in resonance collisions.[5,6] In electron collisions with HCl and HF at low energies, an unusual observation is a strong threshold peak (~10 Å^2) in vibrational excitation[7,8] characterized by isotropic scattering. In dissociative attachment the cross section for Cl^-/HCl[8,9] shows a vertical onset at the lowest dissociation limit of 0.82 eV, with anomalous step-structure at energies coincident with the vibrational thresholds of HCl ($v' = 3, 4, ...$). While extensive theoretical investigations[10,11,12,13] have been made, the physical mechanisms responsible for these structures remain controversial.[14]

In this paper we report experimental results in dissociative attachment from vibrationally and rotationally excited HCl and HF at 0–4 eV. We resolved the vibrational levels and found a strong increase of cross sections for Cl^-/HCl and F^-/HF with vibrational excitation, similar to the case of H_2. Furthermore, we found a pronounced structure in the Cl^- formation cross section from rotationally excited HCl, which is without analogy in the H_2 case. In the present experiment a large range of internuclear separations is probed via excited initial states. These data thus provide new information about the coupling between electronic and nuclear motion unattainable by the previous ground-state studies.

II. EXPERIMENT

The electron impact mass spectrometer used for this investigation was described previously.[3,15] Figure 1 shows a schematic view of the apparatus. It consists of a trochoidal monochromator to form a beam of monoenergetic electrons, a hot iridium collision chamber where the excited molecules are generated, and a quadrupole mass filter to analyze the negative ions resulting from collisions. Standard counting and signal averaging techniques are used for data collection. The collision chamber can be heated with a current of up to 100 A, pulsed at ~20 Hz. Signal acquisition is inhibited during the heating cycle to bypass the interfering effect of the stray magnetic field. The temperature of the collision chamber is monitored with a thermocouple to an accuracy of ±30 °K and the gas is assumed to be in thermal equilibrium with the walls. The arguments and experimental procedures justifying the latter as-

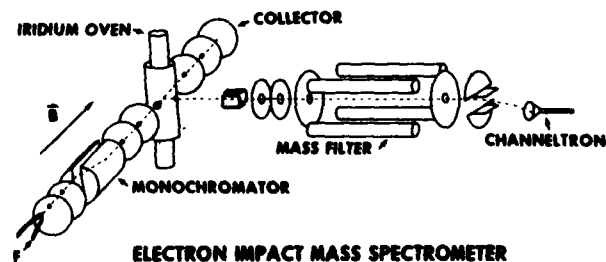FIG. 1. Schematic diagram of electron impact mass spectrometer.
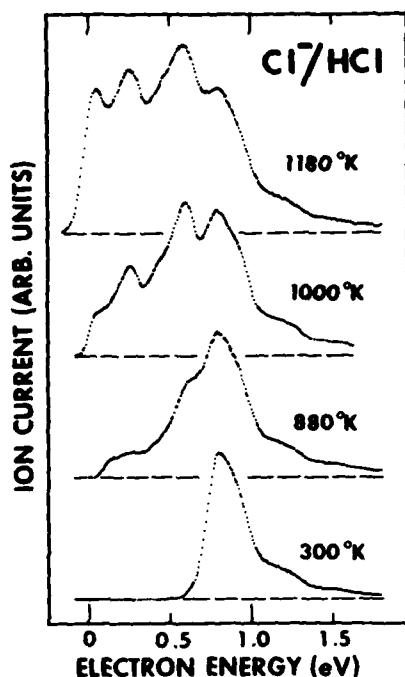
FIG. 2. Energy dependences for Cl⁻ formation by electron impact on HCl at different temperatures. The four spectra have approximately the same vertical scales.

sumption are similar to those given in our earlier work.[3]

The experiment reported here consists of measurement of the energy dependence curves for Cl⁻/HCl, Cl⁻/DCl, and F⁻/HF at temperatures from 300–1200 °K. The energy scale is calibrated at all temperatures with the 3.72 eV onset of H⁻/H$_2$ by admixing molecular hydrogen into the sample gas, and is accurate to ±40 meV. Typical electron-beam current is 10^{-8} A, with energy spread of 50 meV as determined by retardation.

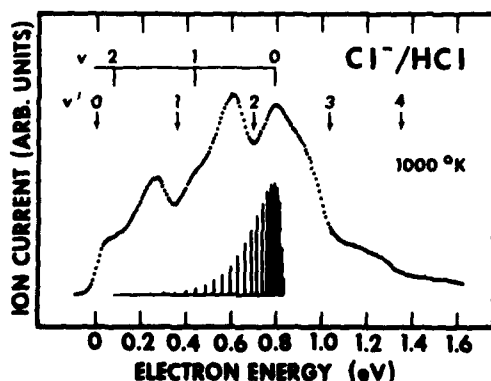FIG. 3. Energy dependence of Cl⁻/HCl in the threshold region at 1000 °K. The vertical bars under the energy-dependence curve give the rotational population and their threshold positions. Expected peak positions from vibrationally excited molecules are marked v. The vibrational-level energies of the neutral HCl molecule are v'. The energy scale is accurate to ±40 meV.
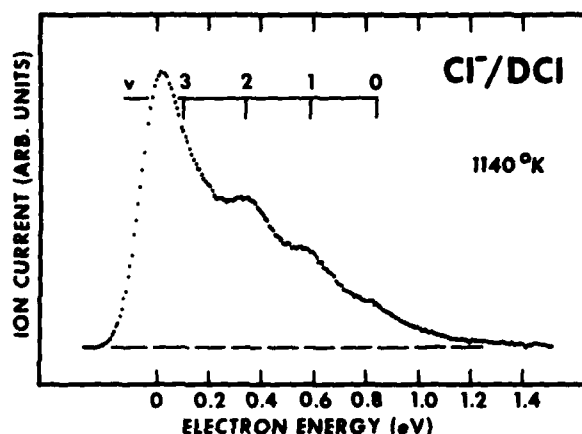

FIG. 4. Energy dependence of Cl⁻/DCl in the threshold region at 1140 °K.

Purity of the sample is monitored via the mass spectrum of positive ions at low and high temperatures. The experiments are performed after passivation of the gas handling system for several days. Positive-ion peaks due to halogen molecules are about 0.1% in HF and undetectable in HCl.

III. RESULTS AND DISCUSSION

Figure 2 shows the energy dependence of Cl⁻ formation from HCl in the 0–2 eV region at four different temperatures between 300 and 1180 °K. The 300 °K spectrum is consistent with the results of previous experiments.[8,9] It has a steep rise with maximum[16] at 0.82 eV, the ground dissociation limit of Cl⁻ + H. Step structures occur in the high-energy tail near 1.03 and 1.35 eV, at which energies the vibrational channels $v' = 3$ and 4 become open. As the temperature is increased, the spectra in Fig. 2 show additional Cl⁻ peaks at lower energies. They are due to rotationally and vibrationally excited HCl, which require less energy to reach the same dissociation limit.

Figure 3 shows a detailed spectrum of Cl⁻/HCl at 1000 °K. At this temperature the most pronounced new features are the two peaks centered about 0.2 eV below the expected onsets for Cl⁻ production from the $v = 0$ and 1 states of HCl. These peaks arise from the increase of cross section with rotational quantum and are shaped by the stepwise drop of cross section at the opening of each vibrational channel of HCl (marked v' in Fig. 3). We shall further discuss this effect later. The signals due to vibrationally excited molecules (marked v in Fig. 3) appear as shoulders in the spectrum.

Figure 4 shows the spectrum obtained with DCl. The increase of Cl⁻ cross section with vibrational excitation is sufficient to make the signal from excited molecules dominate the spectrum. The HF result is shown in Fig. 5. Shoulders due to HF in the $v = 1$ and $v = 2$ states are visible, as are the step structures at the opening of individual vibrational channels.

To determine the cross sections of different vibrational states relative to the ground state, we compare
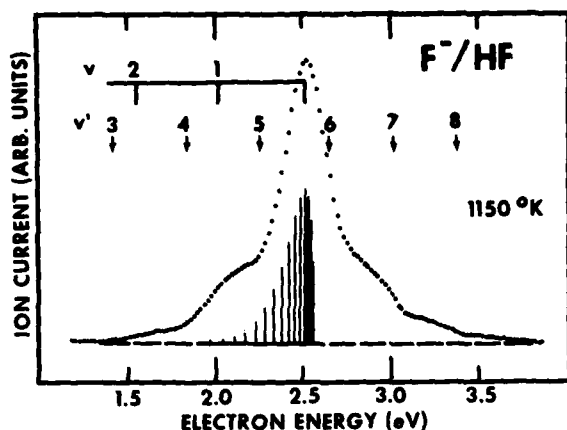
FIG. 5. Energy dependence of F⁻/HF in the threshold region at 1150 K.

the corresponding signal intensities[17] in Figs. 3, 4, and 5 with their thermal population. For example, the population ratio of HCl between $v = 1$ and $v = 0$ is 0.016 at 1000°K. At this temperature the corresponding signal ratio of Cl⁻ obtained from the energy-dependence curve in Fig. 3 is 0.60, yielding $\sigma(v=1)/\sigma(v=0) = 38$ for dissociative attachment in HCl. Table 1 summarizes the relative cross sections for $v = 1$ and $v = 2$ of HCl, DCl, and HF obtained with the above procedure. The main experimental errors arise from the uncertainty in target temperature and the overlap of signals from adjacent rotational-vibrational manifolds in the energy dependence curves (see Fig. 3, 4, and 5). The combined systematic errors are ±30% for $v = 1$ and ±50% for $v = 2$. Statistical errors are negligible.

Extraction of the cross sections for rotational states, unlike their vibrational counterparts, is not done here due to the absence of resolved rotational structure in the dissociative attachment profile. Among the three molecules studied here, HCl yields the most pronounced rotational effect. The energy dependence of Cl⁻/HCl in Fig. 3 shows two broad peaks at 0.60 and 0.25 eV for the rotational manifolds of $v = 0$ and $v = 1$ states. We interpret these features as arising mainly from two effects. The first is a monotonic increase of the cross section with rotational quantum similar to that observed in H_2. Together, this cross section increase and the smooth variation of the rotational state population lead to a broad feature in the Cl⁻/HCl curve. Second, superimposed on this wide feature are sharp drops in cross section at the opening of vibrational excitation channels ($v' = 1$ and 2 in Fig. 3). Step structure at vibrational channels $v' = 3$, 4, ... has been previously observed in the high-energy tail of the Cl⁻ formation from ground-state HCl.[8,9] In our case the rotational excitation lowers the effective threshold for Cl⁻, and the steps due to the $v' = 1$ and $v' = 2$ vibrational channels become visible. These discontinuities occur at nearly the same energy, independent of the initial rotational quantum; they thus enhance[18] each other. We should emphasize that the above interpretation is tentative and detailed understanding of the rotational effects awaits further studies.

In HF a depression is visible at each opening of a vibrational channel (v' in Fig. 5) both on the low- and high-energy sides of the $v = 0$ peak at 2.5 eV. This indicates the presence of an effect similar to HCl, but the spectrum lacks the fine detail found in HCl. In DCl, such an effect appears to be masked by the vibrational enhancement of the cross section.

The observed large increase of cross section with vibrational quantum shows that, like in H_2, dissociative attachment in HCl and HF at low energies is very sensitive to the range of nuclear motion. In H_2 the sensitivity to vibrational quantum was caused[4] by the very short lifetime (10^{-15} sec) of the $^2\Sigma_u^+$ resonant state. This interpretation, however, may not be simply transferred here because of the very different interaction due to the electric dipole moment of these molecules. There is not yet a unique theoretical[14] picture for dissociative attachment and vibrational excitation in HCl at low energies. Nonetheless, much new information on the electronic properties of HCl⁻ have emerged from the recent ab initio calculations.[12,19]

Figure 6 compares the potential-energy curves of H_2 and HCl in the energy region relevant to the dissociative attachment studied here. The $^2\Sigma_u^+$ state of H_2^- in the figure is the short-lived shape resonance[4,5] discussed earlier. The two HCl⁻ curves labelled 1 $^2\Sigma^+$ and 2 $^2\Sigma^+$ were calculated by Taylor et al.[12] with a stabilization method, but no lifetimes were available. The 1 $^2\Sigma^+$ state mimics the neutral curve and dissociate into Cl⁻ + H at 0.82 eV. This state has recently been recalculated by Krauss and Stevens[19] using first-order configuration interaction wavefunctions. With a high flexibility in the basis wavefunctions, the latter authors also found that the HCl⁻ curve mimics the neutral to the left of the crossing point.[20] However, the attached electron cloud is shown to be as diffuse as the basis set permits, without the localized character normally associated with a resonant state.

According to the resonant theory, dissociative attachment in HCl via the 1 $^2\Sigma^+$ state proceeds with electron attachment to the left of the crossing followed by dissociation. In light of the above calculations, electron attachment will be confined to the "mimic" region and thus little, if any, repulsive action can be expected for the HCl⁻ compound. It appears to us that this is in-

TABLE I. Vibrational enhancement in threshold cross section of dissociative attachment.[a,b]

	HCl	DCl	HF
$\sigma_{v=1}/\sigma_{v=0}$	38	32	21
$\sigma_{v=2}/\sigma_{v=0}$	880	580	300

[a]Experimental errors are + 30% for $v = 1$ and + 50% for $v = 2$ for the ratios tabulated above.
[b]The peak cross sections for ground-state ($v = 0$) HCl and DCl were determined to be 8.9×10^{-18} cm² and 1.8×10^{-18} cm², respectively, by Azria et al. (Ref. 21).
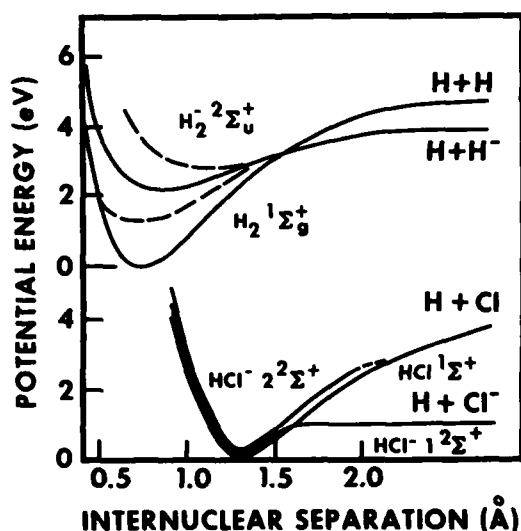
FIG. 6. Comparison of the potential-energy curves for HCl (from Ref. 12) and H_2 (schematic). The two dashed curves roughly show the variation of the width of H_2^- ($^2\Sigma_u^+$) with nuclear separation. Note the different behavior of H_2^- and HCl$^-$ to the left of the crossing between the ion and the neutral curves.

consistent with the large cross section observed. The threshold cross section of Cl$^-$ from ground-state HCl was determined by Azria et al.[21] to be $(8.9 \pm 0.7) \times 10^{-18}$ cm^2. The present experiments yield 38 and 880 times larger magnitudes for the $v = 1$ and 2 states. The threshold cross section of Cl$^-$/HCl ($v = 2$) at 0.1 eV is $(7.8 \pm 4.7) \times 10^{-15}$ cm^2 and becomes comparable to the wavelength-limited cross section[2] (10^{-14} cm^2) for electron capture to the 1 $^2\Sigma^+$ resonance. To reconcile the above observations we note that the conventional theory of dissociative attachment may not be applicable here. At 0.1 eV, the electron energy is comparable to the vibrational energy of HCl, and thus Born-Oppenheimer approximations may break down. As a result, electron attachment could proceed to the *right* of the crossing, and yield Cl$^-$ efficiently.

Such an approach of dissociative attachment using virtual states[11,22] has recently been proposed by Herzenberg.[23] In this theory Cl$^-$ formation occurs to the *right* of the crossing point via nonadiabatic coupling to the nuclear velocities, thereby bypassing the difficulties discussed above. Using the same virtual state previously advanced for vibrational excitation[11] in HCl, Teillet-Billy and Herzenberg[23] have been able to account for the Cl$^-$ formation from ground HCl and DCl. It would be desirable to show whether this approach can also reproduce the present observations, as well as those from the reverse process, associative detachment by thermal Cl$^-$ on H, recently obtained by Zwier et al.[24]

IV. CONCLUSIONS

Electron impact experiments on nuclear excited molecules provide information about the scattering process at an extended region of internuclear separation unattainable to the common ground-state studies. We have

investigated dissociative attachment in nuclear excited HCl and HF. These molecules in the past attracted much interest of experimentalists and theorists because of their unusual scattering properties at low energies.

We find that the cross section for dissociative attachment is very sensitive to the range of nuclear motion, reflected by the large increase of cross section with vibrational excitation. We also find anomalous structure in the cross section of rotationally excited HCl. This structure coincides with the opening of the $v' = 1$ and $v' = 2$ vibrational channels. Both findings demonstrate the need for further theoretical investigation utilizing the new experimental data. The cross sections presented here also provide important information for understanding discharges containing HCl or HF, as in the rare gas halide lasers.[25]

ACKNOWLEDGMENTS

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[16]The position of this Cl$^-$ peak is temperature dependent. As the temperature is increased to 1000 °K, for example, the peak shifts down to 0.80 eV.

[17]We decompose the energy-dependence curves into component curves with $v = 0$, 1, and 2. Each curve contains contributions from many unresolved rotational states and its height yields the relative signal from corresponding vibrational state. The component curves are found to have approximately the same shapes and widths for all vibrational levels, consistent with the observed similarity of the rotational manifolds associated with different vibrational levels in the energy-dependence curves.

[18]The predissociation of a $2^2\Sigma^+$ HCl⁻ state proposed by Taylor *et al.* in Ref. 12 could enhance the peaks around 0.25 and 0.6 eV of the spectrum in Fig. 3. Evidence for such a structure was observed by Azria *et al.* as a weak structure near 0.9 eV in the ground state HCl spectrum. See R. Azria, M. Tronc, Y. LeCoat and D. Simon, abstract of papers, 11th ICPEAC, Kyoto 1979, p. 360.

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Electron-impact excitation of He: Threshold region

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(Received 19 November 1980)

Differential cross sections for excitation to the $n = 2$ states of He are studied with an electron-impact spectrometer from threshold to 4 eV above. We observe pronounced angle-dependent structures in threshold excitation to the $2\,^1P$ state and in near-threshold excitation in the $2\,^3S$ state. Together, these experimental findings and recent theoretical considerations suggest the existence of a new ^2P resonance near 20.8 eV.

Electronic excitation of atoms by electron impact is of intrinsic as well as interdisciplinary (for example, gas lasers, upper atmospheric processes) interest. Despite previous intensive studies,[1] the physical mechanism dominating electronic cross sections in the *threshold region* is, in general, still not well understood.

Recent advances in electron-beam techniques have yielded much new information on total cross sections.[2,3] Quantitative differential cross sections, however, are available only in He due to the more stringent experimental requirements. Previous measurements[4,5] concentrated on the $n = 2$ states: 2^3S, 2^1S, 2^3P, and 2^1P. At impact energies below 22.4 eV, four resonances have been identified[6] to play major roles in these excitation cross sections. They are a $1s2s^2\,^2S$ Feshbach resonance below the 2^3S onset, a ^2S virtual state at the 2^1S threshold, and two core-excited shape resonances, $1s2s2p\,^2P$ and $1s2p^2\,^2D$, below the 2^1P state.

Here we report several new findings in the excitation of the $n = 2$ states of He from threshold to 4 eV above. We show that the differential cross sections for the 1^1S-2^1P and 1^1S-2^3P transitions differ markedly at threshold. For excitation to the 2^3P state, we observe a threshold peak with angle-dependent width. This is not predicted in previous scattering theories,[6] and we interpret it as a resonance-interference effect. We also show that the previously known ^2D resonance peak in the 1^1S-2^3S transition moves in energy with scattering angle, its angular behavior being dominated by both p- and d-wave contributions. To account for these observations we propose a new ^2P shape resonance at 20.8 eV. Using a hyperspherical coordinate approach Watanabe[7] recently showed that this ^2P resonance (second member of $1s2s2p$) lies near this energy, provided that the interchannel coupling is sufficiently strong for it to exist.

The electron-impact spectrometer for the present experiments is a crossed-beam apparatus using hemispherical electrostatic energy analyzers.[8] Several modifications have been made to achieve uniform transmission of scattered electrons at low energies. The acceptance angle of the energy analyzer is made energy insensitive by placing the entrance pupil directly behind the collision region. A liquid-nitrogen-trapped turbo-molecular pump replaces the regular oil diffusion pump, thereby reducing surface contamination by hydrocarbons. Surface conditions of the collision region are stabilized by operating the electrodes at 460 K. Details of these changes are planned to be given in a future paper.

We have measured the absolute differential cross sections for excitation to $n = 2$ states in He at scattering angles 30°–90° with an apparatus resolution about 40 meV. The transmission of the analyzer at different electron energies is controlled by use of the ionization continuum in He.[5,9] Energy-loss spectra of He are measured at several impact energies above the ionization potential. The observations are compared with the expected uniform energy distribution for the two scattered electrons.[10] We estimate that the energy dependences determined for the four $n = 2$ states are accurate to ±20% from 100 meV to 4 eV above threshold. Below 100 meV the energy dependences are only qualitatively correct.

The relative magnitudes among these electronic excitation cross sections are determined by obtaining constant residual-energy spectra at several energies. The absolute magnitudes of the cross sections are obtained by normalizing the 1^1S-2^3S excitation function to the calculated elastic cross sections in He,[11] as previously described.[5] The absolute differential cross sections obtained are accurate to ±30%.

Figures 1 and 2 show our measured absolute differential cross sections for excitation to the $n = 2$ states within 4 eV of threshold at two selected angles. The magnitudes of the peak cross sections are in quantitative agreement with earlier experiments[5,12] but agreement on the exact shapes is only within a factor of 2. In this letter we shall concentrate on the *new features* observed below 22.4 eV, the onset of the $n = 3$ Feshbach reso-
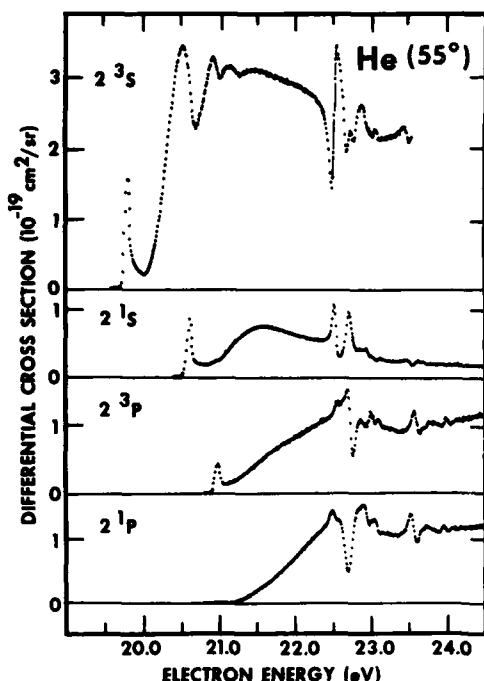
FIG. 1. Absolute differential cross sections for the $n = 2$ states of He at 55°. At this angle resonances of ^2D symmetry contribute negligibly to the 2^3S and 2^1S cross sections. Notice the threshold peak in the 2^3P cross section and the gradual onset in the 2^1P cross section. The structures above 22.4 eV are Feshbach resonances associated with the $n = 3$ states.

FIG. 2. Absolute differential cross sections for the $n = 2$ states of He at 90°. At this angle resonances of ^2P symmetry contribute negligibly to the 2^3S and 2^1S cross sections. The threshold peak observed in the 2^3P cross section at low angles appears as a step here, while the threshold feature in 2^1P remains unchanged.

nances.

Unlike previous experiments,[4,5] the present results establish contrasting threshold behavior for excitation to the 2^1P and 2^3P states. Whereas the 1^1S-2^1P cross sections show a gradual onset at all angles (30°–90°), those for 1^1S-2^3P yield a threshold peak at low angles, systematically changing to a threshold step at 90° (see Figs. 1 and 2). This strong threshold excitation to the 2^3P state is not predicted by the differential cross section calculations of Fon et al.[6] It is hinted in the total cross section calculation of Oberoi and Nesbet,[6] in which the excitation to 2^3P rises much faster than that to the 2^1P state.

Angular variation of the width of a threshold peak has been observed previously in the 1^1S-2^3S transition. This was understood to arise from interference[6] between the tail of the ^2S Feshbach resonance and the ^2P and ^2D scattering states in the threshold region. The present observation in the 1^1S-2^3P transition suggests similar interference between the known ^2P (20.3-eV) resonance and a new ^2P (20.8-eV) shape resonance (to be discussed below) and the ^2D scattering state.[14]
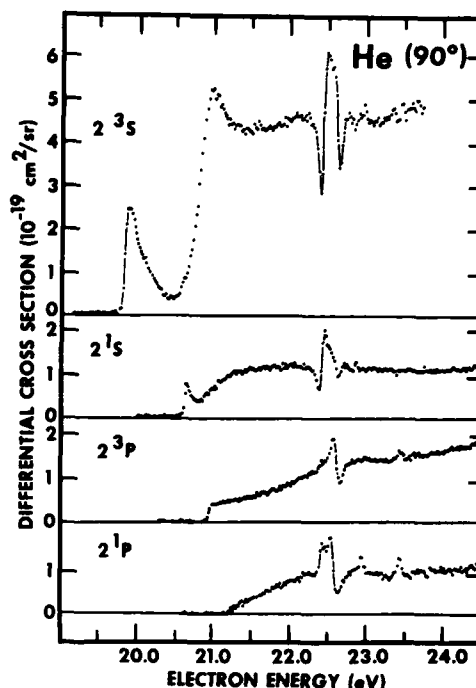
A marked angular effect is observed in the dif-

ferential cross sections for excitation to the 2^3S state. Figure 3 shows several energy dependence curves obtained at scattering angles around 55°. The first peak at 20.5 eV, previously identified as a ^2P shape resonance is unshifted with angle, and shows p-wave angular behavior. The second peak, which was identified[6] as a ^2D resonance shifts to lower energy with decreasing scattering angle. While at high angles (70°–90°) its angular behavior is consistent with d-wave scattering, this peak is clearly visible at 55° (see Fig. 3) where the contribution of the ^2D resonance to the 1^1S-2^3S transition should be negligible. At low scattering angles (40°–30°), the relative intensity of this peak and the first ^2P peak is nearly constant. These observations show the strong effect of the ^2P scattering state between the ^2P (20.3 eV) and ^2D (21.0 eV) resonances. We interpret this in terms of the dominant role in 1^1S-2^3S excitation of a new ^2P resonance at those energies. Applying a resonance profile analysis to this unresolved peak at various angles, we determine the center of this proposed ^2P resonance to be at 20.8 eV and its width to be comparable to that of the known ^2P resonance ($\Gamma \sim 0.4$ eV).[6]
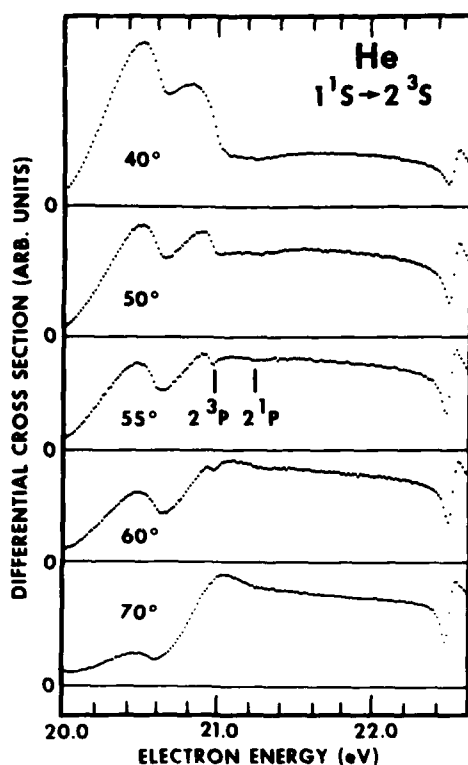
FIG. 3. Energy dependence curves for the 1^1S-2^3S transition of He at angles near 55°. Note that the position of the 20.5 eV peak is unchanged with angle, but the 21.0 eV peak at 70° moves to about 20.8 eV at 40°. Wigner cusps are apparent at the onsets of 2^3P and 2^1P states and are especially pronounced at 55°.

TABLE I. Core-excited shape resonances ($n =2$) accessible by electron impact on He (energies in eV).

| | $1s2s2p$ | | $1s2p^2$ | |
	^2P	^2P	^2D	^2S
Previous work (Refs. 4,5,6)	20.3		21.0	
"Be model" (Ref. 13)	20.1	20.7	21.1	21.6
Hyperspherical coordinate method (Ref. 7)	20.5	20.5–20.96 [a]	b	b
Present experiment	20.5	20.8	21.0	b

[a] Resonance lies within this range, if it exists.
[b] Not studied in present work.

In Table I we list the four possible core-excited shape resonances (configurations $1s2s2p$ and $1s2p^2$) that are accessible by electron impact on He. Only the ^2D and one of the two ^2P resonances have been discussed in earlier work. To assess the possibility of another ^2P resonance at about 20.8 eV, we examine the energies of the states of Be having electron configurations $1s^22s2p$ and $1s^22p^2$. To obtain the energies of the corresponding He$^-$ states, we (1) divide the energy above the ground state of each Be level by 4 to compensate for its greater core charge, and (2) assign ground-state Be $(1s^22s^2)$ the energy of He$^-$ $(1s2s^2)$—the ^2S Feshbach resonance at 19.34 eV. The resulting energies are indicated in Table I under "Be model." There is good agreement between our observations and the predictions.[13]

The resonance energies listed in row 3 of Table I are obtained by Watanabe[7] using the hyperspherical coordinate approach. This method interprets the doublet resonances of He as manifestations of strong nonadiabatic coupling between the adiabatic potential curves converging to the various $n = 2$ levels of He. The results of this calculation predict that the lower ^2P resonance is at 20.5 eV and that the higher ^2P resonance is between 20.5 and 20.96 eV, in agreement with our results. However, the latter resonance exists only if the interchannel coupling is sufficiently strong. The possible fulfillment of this condition is still under investigation.

An earlier scattering calculation of Berrington *et al.*[15] also indicates the importance of the ^2P scattering state near 20.9 eV. In the elastic 2^3S-2^3S cross section these authors observe "a second ^2P peak above the 2^1S threshold perhaps indicating that the rise in the eigenphase," which they calculate "in this energy region may be associated with another resonant or virtual state of He$^-$."

In conclusion, our present observations indicate that the ^2P scattering state plays a dominant role in excitation to the 2^3S and 2^3P states. These observations, together with the above theoretical considerations suggest a new broad $1s2s2p$ ^2P resonance at 20.8 eV, in addition to the known ^2P resonance (20.3 eV).

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[14]In an S-P transition the ^2P partial cross section is isotropic while the ^2D contribution has angular dependence $(1+1.2\cos^2\theta)$. Qualitative agreement with the experiment is obtained if these partial cross sections are assumed to obey the Wigner threshold law, i.e., $\sigma_{l=1}\propto E^{1/2}$ (outgoing s electron) and $\sigma_{l=2}\propto E^{3/2}$ (outgoing p electron).

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